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Original Article

Order–disorder phase transitions in thin films described by transverse Ising model

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ABSTRACT

The order–disorder phase transition in thin films at finite temperature and zero temperature (quantum phase transition) is discussed within the transverse Ising model using molecular field approximation. Experimentally, it is shown that the Curie temperature T_C of perovskite $PbTiO_3$ ultra-thin film decreases with decreasing film thickness. We obtain an equation for T_C of thin film in external magnetic and transverse fields. Our equation explains well for the case of strong transverse strain field this behaviour.

1. Introduction

Nanoscale materials like ferroelectric (FE) and ferromagnetic (FM) ultra-thin films now are important classes of materials which have been used for making of new electronic devices (see reviews [1,2]). In order to understand properties of thin films, some traditional models for bulks like Heisenberg, XY, Ising one are applied and solved by different theoretical methods (see for example, review [3] on the case of frustrated thin films). According to the Mermin–Wagner theorem [4], 2D Heisenberg model with isotropic short range exchange interaction has no long range order at finite nonzero temperature. Thin films are quasi two dimension case when the condition of the Mermin–Wagner theorem may be violated by presence of anisotropic exchange between layers, crystallographic anisotropy … Among anisotropic models, the transverse Ising model (TIM) plays essential role because of its simplicity and usefulness for explanation of wide classes of phase transitions including quantum phase transition [5]. De Gennes firstly introduced the transverse Ising spin 1/2 model for description of FE phase of KDP [6]. TIM is solved exactly for one dimensional spin 1/2 chain [5], but not for the 2D and thin film cases. Several authors have used TIM for calculation of such as: thin films and FE particles within MFA [7,8]; FM magnetization in a thin film within effective field approximation [9]; influence of layer defect on the damping in FE thin films [10]. In previous works, nature of the transversal field that plays important role in damping of order–disorder phase transition temperature was briefly investigated. Quantum phase transition (QPT) in transverse Ising model for thin films is also not well examined according to our awareness, even in MFA. Aim of this research is to use TIM for study order–disorder phase transitions in thin films at finite and zero (QPT) temperatures and to describe thickness dependence of the Curie temperature in ultrathin $PbTiO_3$ films within MFA. The QPT case is derived from finite temperature results in the limit $T \to 0$.

2. Film model and mean field approximation

Following [11], we consider cubic spin lattice of a thin film, which consists of n spin layers and there are N spins in every layer. The Oz axis of the crystallographic coordinate system is directed perpendicularly to the film surfaces and the spin layers are parallel to xOy plane (see Fig. 1).

A spin position in the lattice is shown by the lattice vector (denoted by νj) where ν is the layer index($\nu = 1, \ldots, n$), $\mathbf{R}_j$ is the two-component vector denoting the position of the jth spin in this layer. Vector $\hat{\mathbf{z}}$ is unit vector directed along Oz axis, and a is the spin lattice constant (in the rest of this paper, this quantity is taken to be 1 and all the lengths are measured in unit of lattice constant). The transverse Ising Hamiltonian for the spin film system is written as:

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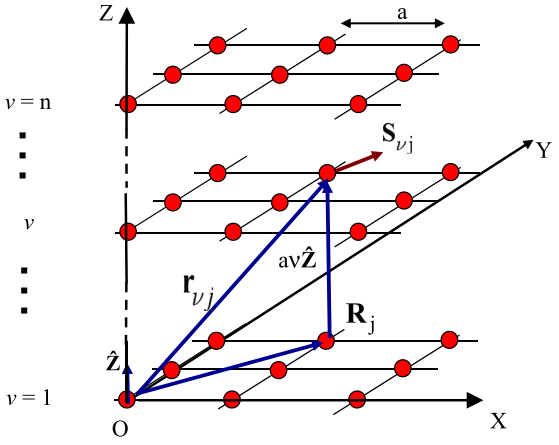

Fig.1. Position vector of a spin $\mathbf{r}_{\nu j} = \mathbf{R}_j + a\nu\hat{\mathbf{Z}}$ in the cubic spin lattice.

$$H = -\mu h \sum_{\nu j} S^z_{\nu j} - \Omega \sum_{\nu j} S^x_{\nu j} - \frac{1}{2} \sum_{\nu j,\nu' j'} J_{\nu\nu'}(\mathbf{R}_j - \mathbf{R}_{j'}) S^z_{\nu j} S^z_{\nu' j'}, \tag{1}$$

where the first (second) term of (1) corresponds to the energy of the spin system in the longitudinal (transversal) field h (Ω). The third term is Ising type exchange interaction between spins.

In the mean field approximation (MFA), where spin fluctuation $\delta S^z_{\nu j} = S^z_{\nu j} - \langle S^z_\nu \rangle$ is neglected, Hamiltonian (1) is rewritten as

$$H_{MF} = \frac{N}{2} \sum_{\nu,\nu'} J_{\nu\nu'}(0) \langle S^z_\nu \rangle \langle S^z_{\nu'} \rangle - \mu \sum_{\nu j} h_\nu S^z_{\nu j} - \Omega \sum_{\nu j} S^x_{\nu j}, \tag{2a}$$

$$J_{\nu\nu'}(\mathbf{k}) = \sum_j J_{\nu\nu'}(\mathbf{R}_j) e^{i\mathbf{k}\mathbf{R}_j}. \tag{2b}$$

Brackets $\langle \ldots \rangle$ mean the thermodynamic average and $\beta^{-1} = k_B T$. The effective field h_ν acting on the spin at the layer ν is given by

$$h_\nu = h + \mu^{-1} \sum_{\nu'} J_{\nu\nu'}(0) \langle S^z_{\nu'} \rangle. \tag{3}$$

$J_{\nu\nu'}(\mathbf{k})$is a Fourier image of the nearest neighbour (NN) spin exchange $J_{\nu\nu'}(\mathbf{R}_j)$. Denoting J (J_p) the exchange strength between in-plane (out-of-plane) NN spins, one has

$$J_{\nu\nu'}(\mathbf{k}) = z_s J \xi(\mathbf{k}) \delta_{\nu\nu'} + J_p(\delta_{\nu',\nu+1} + \delta_{\nu',\nu-1}), \tag{4a}$$

$$\xi(\mathbf{k}) = \frac{1}{z_s} \sum_j e^{i\mathbf{k}\mathbf{R}_j} \tag{4b}$$

z_s ($2p$) stands for the in-plane (out-of-plane) NN spin number and $z_s + 2p = Z$ denotes the total NN number for a given spin in the bulk spin lattice. For simple cubic spin lattice $z_s = 4$ and $p = 1$. H_{MF} can be diagonalized easily by the well-known unitary transformation of spin operators (see [5])

$$S^x_{\nu j} = \frac{h_\nu}{\gamma_\nu} S^{x'}_{\nu j} + \frac{\Omega}{\mu\gamma_\nu} S^{z'}_{\nu j}; \quad S^z_{\nu j} = -\frac{\Omega}{\mu\gamma_\nu} S^{x'}_{\nu j} + \frac{h_\nu}{\gamma_\nu} S^{z'}_{\nu j}; \quad \gamma_\nu = \sqrt{h_\nu^2 + \left(\frac{\Omega}{\mu}\right)^2}, \tag{5}$$

$$H_{MF} = \frac{N}{2} \sum_{\nu,\nu'} J_{\nu\nu'}(0) \langle S^z_\nu \rangle \langle S^z_{\nu'} \rangle - \mu \sum_{\nu j} \gamma_\nu S^{z'}_{\nu j}. \tag{6}$$

2.1. Equations of state at finite temperature

It is easy to see from the Equation (6) that γ_ν plays a role of an effective field acting on the spin $S^{z'}_{\nu j}$ similar to h_ν in the Equation (2a). One gets the free energy in MFA as

$$F = -\frac{1}{\beta} \ln\left(\mathrm{Spe}^{-\beta H_{MF}}\right),$$

$$F = \frac{N}{2} \sum_{\nu,\nu'} J_{\nu\nu'}(0) m_{z\nu} m_{z\nu'} - \frac{N}{\beta} \sum_\nu \ln \frac{\mathrm{sh}(S + 1/2) Y_\nu}{\mathrm{sh}\frac{Y_\nu}{2}}, \tag{7}$$

$$Y_\nu = \beta\mu\gamma_\nu. \tag{8}$$

Here and in the following parts we denote average of the spin components per site at layer ν as $m_{z\nu} = \langle S^z_\nu \rangle, m_{x\nu} = \langle S^x_\nu \rangle$. MFA equations for components of order parameter of the spin system at finite temperature can be found from minimum condition of the free energy (7)

$$m_{z\nu} = \frac{h_\nu}{\gamma_\nu} b_S(Y_\nu), \tag{9a}$$

$$m_{x\nu} = \frac{\Omega}{\mu\gamma_\nu} b_S(Y_\nu). \tag{9b}$$

Here $b_S(x)$ is the Brillouin function

$$b_S(x) = \left(S + \frac{1}{2}\right) \coth\left(S + \frac{1}{2}\right) x - \frac{1}{2} \coth\frac{x}{2}. \tag{10}$$

MFA equations of state (9a, b) for components of layer magnetic moments of thin films can be derived in another way by realizing that in new prime"'" representation (5)

$$\left\langle S^{x'}_{\nu j} \right\rangle = 0; \quad \left\langle S^{z'}_{\nu j} \right\rangle = b_S(Y_\nu). \tag{11}$$

Close to the order–disorder phase transition temperature (the Curie temperature T_C), the spin system is unstable and the magnetic moment at layer ν (proportional to internal molecular field) is small and may be neglected comparing with the longitudinal field h, and transversal field Ω. Then Equation (9a) reduces to

$$\sum_{\nu'=1}^{n} \left\{ \delta_{\nu\nu'} - \frac{b_S(\beta_c f)}{f} J_{\nu\nu'}(0) \right\} m_{z\nu'} = 0, \tag{12a}$$

$$m_{z,0} = m_{z,n+1} = 0, \tag{12b}$$

$$f = \sqrt{(\mu h)^2 + \Omega^2}; \quad \beta_c = (k_B T_c)^{-1}. \tag{12c}$$

To have non-trivial solution of the system of linear algebraic Equation (12a), the determinant of the Toeplitz-type tridiagonal matrix D_n must be zero,

$$\det D_n = \det \begin{bmatrix} a & c & 0 & 0 & \ldots & 0 & 0 \\ c & a & c & 0 & \ldots & 0 & 0 \\ 0 & c & a & c & \ldots & 0 & 0 \\ . & . & . & . & \ldots & . & . \\ 0 & 0 & 0 & 0 & \ldots & a & c \\ 0 & 0 & 0 & 0 & \ldots & c & a \end{bmatrix} = 0, \tag{13a}$$

where $a = 1 - \dfrac{b_S(\beta_c f) z_s J}{f}$, and $c = -b_S(\beta_c f) \dfrac{J_p}{f}$. (13b)

Determinant Equation (13a) reduces to the eigenvalue problem of tridiagonal matrix D_n (see for example [12]) and one has

$$1 = b_S(\beta_c f)\frac{J}{f}\left[z_s - 2p\eta\cos\left(\frac{\pi\nu}{n+1}\right)\right]. \tag{14}$$

here $\nu = 1,2,\ldots n$. In order to have corresponding expression for 3D limiting case, when $n\to\infty$, it is necessary to chose $\nu = n$ in (14). Finally, one obtain the equation for Curie temperature

$$1 = b_S(\beta_c f)\frac{J}{f}\left[z_s + 2p\eta\cos\left(\frac{\pi}{n+1}\right)\right]. \tag{15}$$

Equation (15) is the explicit MFA equation for the Curie temperature of TIM with arbitrary spin comparing with the S = 1/2 case [8]. It is seen from (15) that the Curie temperature is a function of the longitudinal and transverse field f (see (12c)) and anisotropic exchanges. For the case of small transversal field ($\Omega \ll k_B T_c$) and zero longitudinal field ($h = 0, f = \Omega$), an expansion for the Brillouin function $b_S(x) = S(S+1)x/3$ may be used, and the formula (15) reduces to MFA result for T_c of Heisenberg ferromagnetic thin films given by [13]

$$\frac{k_B T_c}{J} = \frac{S(S+1)}{3}\left[z_s + 2p\eta\cos\left(\frac{\pi}{n+1}\right)\right] \tag{16}$$

Formula (16) is also correct for TIM when both field energies are small in comparison with Curie temperature energy ($\mu h, \Omega \ll k_B T_c$).

At some critical value of the transversal field, the Curie temperature of the n-layer film reduces to zero, $T_c(\Omega_c) = 0$. One gets for $h = 0$ case

$$\frac{\Omega_c}{JS} = z_s + 2p\eta\cos\left(\frac{\pi}{n+1}\right) \tag{17}$$

Denoting $\Delta T_c = T_c^b - T_c$ ($\Delta\Omega_c = \Omega_c^b - \Omega_c$), where the Curie temperature T_c^b (the critical transversal field Ω_c^b) of bulk is obtained from Equation (16) (Equation (17)) in the $n\to\infty$ limit, we can get for the weak transversal field case

$$\frac{k_B \Delta T_c}{J} \approx \frac{2S(S+1)}{3}\eta\left[1 - \cos\left(\frac{\pi}{n+1}\right)\right] \tag{18a}$$

$$k_B \Delta T_c \approx \frac{S+1}{3}\Delta\Omega_c, \tag{18b}$$

$$\Omega \ll k_B T_c. \tag{18c}$$

According to (18a–c), (19) for small transversal field, changes of Curie temperature and critical transversal field from their bulk values are mutual linear dependent.

2.2. Ground state at zero temperature

In order to examine QFT in thin films, one needs to obtain the ground state free energy and equations of states at zero temperature. Taking limit $T\to 0(\beta\to\infty, b_S(\beta\mu\gamma_\nu)\to S)$ in the formulae (7)–(9a, b), we have

$$F_0 = \frac{N}{2}\sum_{\nu,\nu'} J_{\nu\nu'}(0) m_{z\nu} m_{z\nu'} - NS\mu\sum_{\nu}\gamma_\nu, \tag{19}$$

$$m_{z\nu} = \frac{Sh_\nu}{\gamma_\nu}, \tag{20}$$

$$m_{x\nu} = \frac{S\Omega}{\mu\gamma_\nu}. \tag{21}$$

We note that expression $m_{z\nu}$, $m_{x\nu}$ figured in the formulae (19) to (21) are zero temperature components of the spin moment. From Equation (20) we can obtain the same formula (17) for the critical

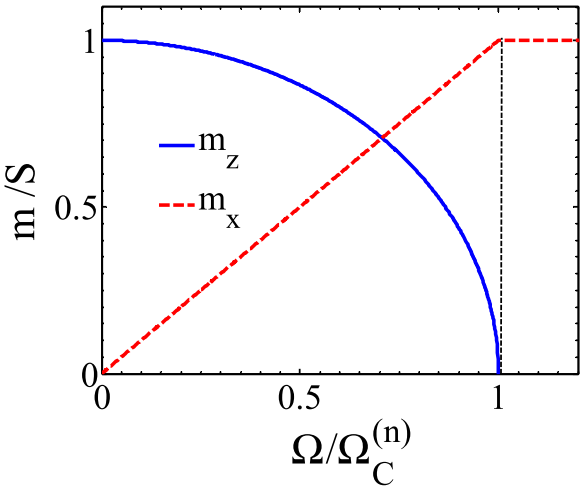

Fig. 3. Dependence of the components of the average spin moment per site of monolayer (n = 1) or symmetric double layer (n = 2) films on the relative transversal field strength. $\Omega_c^{(n)}$ is critical transversal field given by the formula (17) when $h = 0$ (see text).

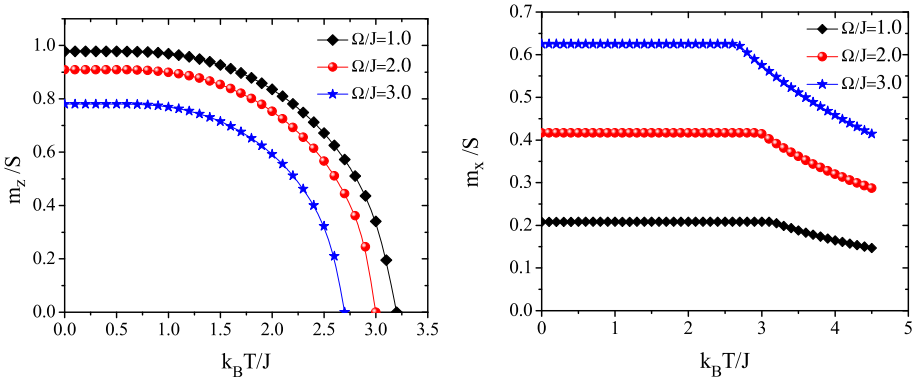

Fig. 2. Temperature dependence of the relative components of the spin moment per site ($m_z/S, m_x/S$) for double layer thin film with two identical surfaces with $\eta = 0.8$, $S = 1$.

transversal field using condition $m_{zv}(\Omega_c) = 0$. The formula (17) is obtained firstly for the critical values of transversal field of TIM, it is valid for description of finite temperature order–disorder transition or QPT in both bulk or thin films at MFA level.

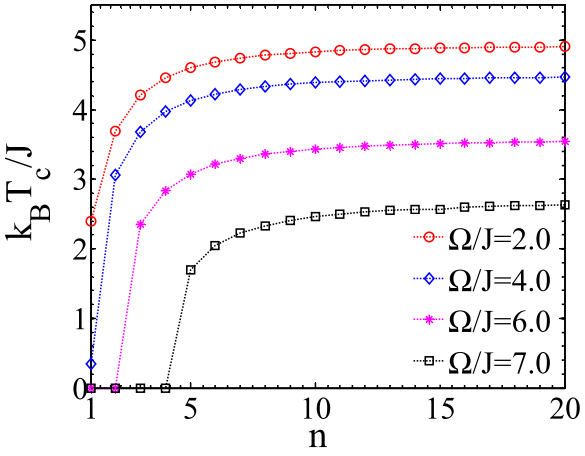

Fig. 4. Thickness dependence of the Curie temperature of cubic spin lattice thin films. Parameters are S = 1, η = 1.8, $h = 0$ (dashed lines connecting points are drawn for better view).

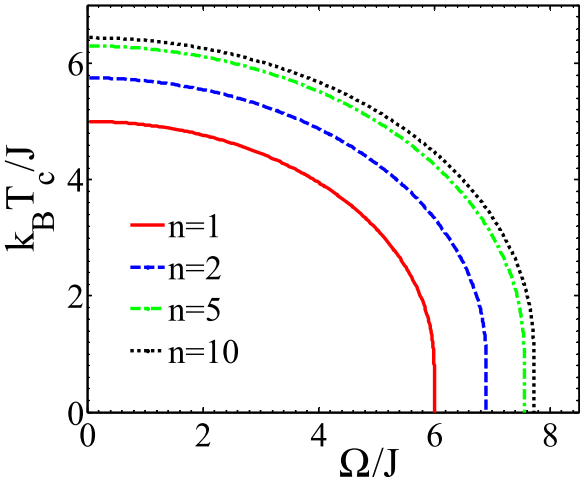

Fig. 5. The Curie temperature of several thin films as a function of the transversal field (S = 1, η = 1.2, $h = 0$).

3. Numerical calculation and comparison with experiment for T_c

In this part we perform the numerical calculation for cubic spin lattice $(z_s = 4, p = 1)$ to show influence of the fields and other factors like thickness, anisotropic behaviour of exchanges on the phase transition in simple cubic spin lattice ultra-thin films. All energy quantities in figures are expressed in unit of the in-plane exchange energy J.

Fig. 2 presents the thermomagnetic-plots of the relative spin components of the symmetric two layer films (the plots for monolayer have similar shapes, but with different T_C). One sees that the increasing transversal field leads to a reduction of m_z but an increase in m_x. Fig. 3 shows these relative spin components as functions of the relative transversal field at $T = 0$ or QPT case. The critical transversal field for monolayer (double layer with anisotropic exchanges) is $\Omega_c^{(1)} = 4JS$ $(\Omega_c^{(2)} = (4+\eta)JS)$ according to Equation (17). It is clear that Fig. 3 has general feature for mono- and double layer films (all plots do not depend on the spin S, J, η, and Z).

Fig. 4 shows the film thickness dependence of Curie temperature calculated by (15) for given ratio of out-of-plane and in-plane exchanges η. Increase of the transversal field causes strong damping of Curie temperature.

Fig. 5 shows the dependence of the Curie temperature on transverse field strength calculated by (15) for η = 1.2. On sees increase of the transversal field leads to suppression of order in thin films, and there is no order for given thin film when $\Omega \geq \Omega_C$.

Fig. 6 illustrates dependence of the critical transversal field Ω_C on the film layer number n for different spin values S = 1 and 3/2 calculated according to Equation (17). The tendency of Ω_C to increase with film thickness is similar to that of the Curie temperature.

Order–disorder phase transition described by TIM can be used for description of ferroelectric-paraelectric (FE-PE) phase transition in FE perovskites where the pseudo-spin has meaning the electrical dipole moment. Equation (15) and its numerical consequence expressed in Figs. 4 and 5 may be used to interpret the measured thickness dependence of the Curie temperature of lead titanate ($PbTiO_3$) ferroelectric thin films (see [14] and cited references therein). It is well-known that stoichiometric unstrained $PbTiO_3$ bulk has order (FE)–disorder (paraelectric-PE) phase transition around 763 K. But in the thin films where thickness consists from few to 100 unit cells, there is strong deviation of T_c from its unstrained bulk value [14] (T_c of films varies in the interval 900–500 K). Surface reconstruction of atomic layers observed in experiment has origin of increasing intrinsic strain with reduction of the film thickness and it is probably sufficient large in few-layer

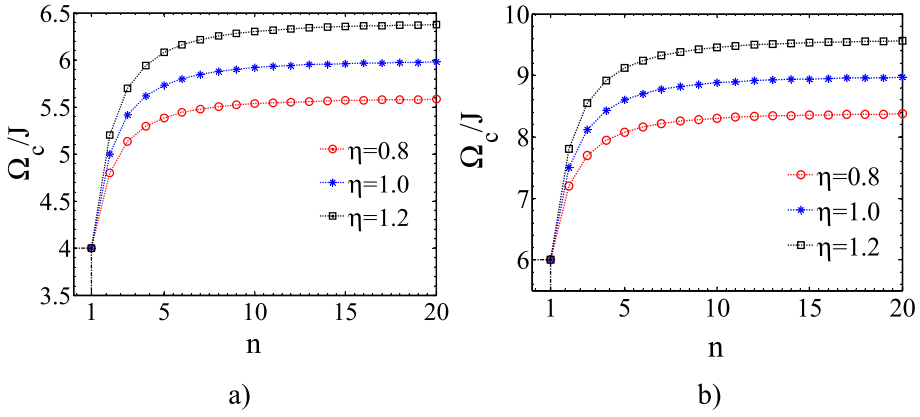

Fig. 6. Dependence of the critical transversal field on the film thickness for different spin S and anisotropic exchange constant η values: S = 1 (a), S = 3/2 (b).

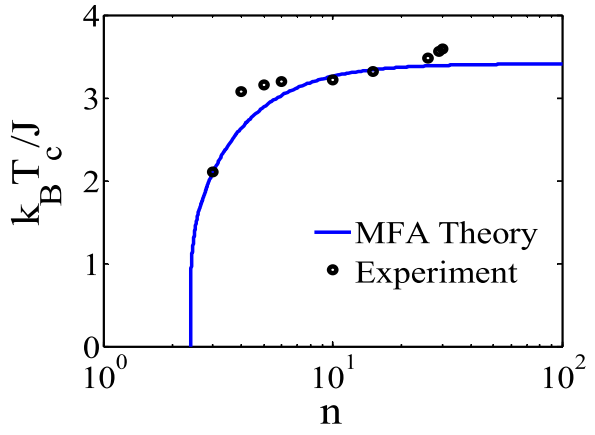

Fig. 7. Theoretical fitting curve for experimental data of thin perovskite $PbTiO_3$ films [14]. Parameters of theory are: $\Omega/J = 6.1$, $\eta = 1.75$, $S = 1$, and n is number of unit cells or number of pseudo-spin layers.

ultra-thin film. Because of that strain, the in-plane exchange between spins is smaller than the perpendicular one. During framework of TIM, one can suggest the film in-plane strain to be equivalent to large, constant transversal field Ω along x direction in film plane. Fig. 7 presents good coincidence between the theoretical MFA curve and experimental data for the $PbTiO_3$ perovskite measured in [14] when parameters are chosen as $\Omega/J = 6.1$, $\eta = 1.75$, $S = 1$.

Investigation on influence of fluctuation on the local moment inside thin films and T_c beyond MFA using method of [11] is aim of our future work.

4. Conclusion

In this contribution we have applied the transverse Ising model for description of the order–disorder phase transition, QPT in thin films within MFA. The expressions for Curie temperature, and critical transversal field are given more explicitly comparing with previous results. Its usefulness is shown by application to describe well thickness dependence of the Curie temperature observed experimentally in $PbTiO_3$ perovskite thin films.

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